Structural study and electrical properties of Zr-doped $Nd_2Sn_2O_7$ pyrochlore compounds

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Abstract. $Nd_2Sn_2O_7$ pyrochlores with the substitution of Zr^{4+} were prepared by conventional ceramic double sintering technique. The single-phase formation was confirmed by X-ray diffraction and neutron diffraction techniques. Relative intensity calculations for X-ray diffraction analysis were performed for oxygen positional parameters $x = 0.331$ and 0.375, while Rietveld refinements were employed for neutron diffraction data. The neutron diffraction study revealed that there are only two anion sites with 48f and 8b positions. This indicates that the 8a site, i.e. O(3) sublattice, is completely vacant and the structure is a perfect cubic pyrochlore with space group Fd3m (O_h^7).

From the conductivity measurements, it is observed that the electronic conductivity dominates from room temperature up to about 525 K and for $T > 525$ K, the oxygen ion conduction dominates the charge transport in these compositions. Complex impedance spectroscopy indicates the existence of grain and grain boundary as two separate elements.

Keywords. Pyrochlores; neutron diffraction; complex impedance spectroscopy.

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1. Introduction

Among the ternary metallic oxides, compounds possessing the mineral pyrochlore structure with a general formula $A_2B_2O_7$ form a family of compounds. The element A is a rare earth or an element with an oxidation state of 2+ or 3+. The element B has to have an oxidation state of 5+ or 4+ for charge neutrality. Thus one may expect metallic behavior in some of these compounds. With varying compositions, ionic conduction or insulating behavior occurs in some of them. In some cases replacing A or B with a rare earth or transition metal has given rise to different types of magnetic behavior.

Pyrochlore oxides are of interest because of their catalytic activity for a variety of processes and high temperature stability [1]. Recent interest in the stannate and

zirconate pyrochlores has stemmed from their potential use as high temperature gas sensors or fast ion conductors. Also these compounds find potential nuclear applications as neutron absorbers and radioactive waste forms for final disposal [2,3].

The cubic pyrochlore structure, space group Fd3m, has eight molecules of the general formula $A_2B_2O_6O'$ in the unit cell. The anion array consists of three independent sites O(1), O(2) and O(3), occupying the locations 48f, 8a and 8b respectively, of which 8b is unoccupied in a fully ordered pyrochlore [4]. The four unique atoms A, B, O and O' have the following positions: A at (0.5, 0.5, 0.5) occupying the 16d sites, B at (0, 0, 0) occupying the 16c sites, O', i.e. O(1) at $(x, 0.125, 0.125)$ occupying the 48f sites and O', i.e. O(2) at (0.375, 0.375, 0.375) occupying the 8b site. The larger A cations are coordinated to six O(1) atoms and two O(2) atoms forming an axially compressed scalenohedron. The smaller B cations are coordinated to six O(1) atoms at equal distances in trigonal antiprisms. The O(1) atoms are bonded to two A and two B cations. The O(2) atom is bonded only to the A cations.

The ionic radius ratio of large cation to small cation and the oxygen parameter x are observed to be a crucial parameter in deciding the stability of the pyrochlore structure [4]. In the present study, we expect that the substitution of Zr^{4+} for Sn^{4+} may induce structural changes in the $Nd_2Sn_{2-y}Zr_yO_7$ system. Therefore, we study stannate–zirconate pyrochlore to find out the effect of Zr doping on the structural stability and electronic state of the materials and also to understand the effect of temperature on electron transport properties of these compounds.

2. Experimental details

Polycrystalline samples of $Nd_2Sn_{2-y}Zr_yO_7$ (with $y = 0.0$–1.0 in steps of 0.2) pyrochlores were prepared by conventional double sintering solid-state reaction of SnO_2 and ZrO_2 with the appropriate neodymium oxide (Nd_2O_3), with intermediate regrinding, or until powder X-ray diffraction did not show the presence of any material other than the desired pyrochlore.

The powder neutron diffraction patterns for $y = 0.0$, 0.2 and 0.4 were collected at room temperature using neutrons of wavelength 1.2421 Å in 0.03 steps on PSD based powder diffractometer at Dhruva reactor, BARC, Mumbai. The values of the occupancy parameters were calculated as occupancy parameter is equal to the number of atoms in a unit cell divided by the total number of available sites in a unit cell. For example, occupancy parameter for $Nd = (16/192) = 0.0833$. Similarly, for other atoms, occupancy parameters were calculated. Least square structure refinements were performed with a PC version of the Rietveld analysis program DBWS-9411. During the refinements, the occupancy parameters for Nd, Sn and Zr (i.e. n_{Nd}, n_{Sn} and n_{Zr}) were kept fixed whereas the occupancy parameters for O(1) and O(2) (i.e. n_{O1} and n_{O2}) were varied. Refinements were continued until the parameter shifts in the last cycle were less than 10%.

Preliminary powder X-ray diffraction measurements were performed on computerized X-ray diffractometer (Phillips model PW-1710) using CuK_α radiation.

The DC electrical conductivity as a function of temperature was measured in the temperature range from room temperature to 800 K, to probe the electronic

state. To understand the nature of conduction, complex impedance measurements are carried out at different temperatures, using Hewlett Packard LCR-Q precision meter (Model 4284A).

3. Results and discussions

Figure 1 shows a typical plot of observed, calculated and difference profiles for the Rietveld refinements from the neutron diffraction data on parent compound $Nd_2Sn_2O_7$. In all cases, the agreement between the observed and calculated profiles is excellent. The structure confirms to the space group Fd3m (O_h^7) of cubic pyrochlore structure. Room temperature structural and temperature factors obtained from Rietveld profile refinement for $Nd_2Sn_{2-y}Zr_yO_7$ with $y = 0.0, 0.2$ and 0.4 are shown in table 1. The values obtained for the cubic lattice parameters are in good agreement with the values obtained earlier by Kennedy *et al* [5]. The size of Zr^{4+} being larger than that of Sn^{4+}, the cell constant was found to increase with Zr^{4+} doping. From the observations of values of occupancy parameter n_{Zr}, Zr is found to occupy the Sn site. Further, as Zr is tetravalent, it occupies the site of Sn^{4+} easily. This result is similar to the observations on $Y_2(Ti_{1-y}Zr_y)_2O_7$ system for $Zr = 0.6$ (6). We have obtained X-ray diffraction patterns for all the compositions of system $Nd_2Sn_{2-y}Zr_yO_7$, with $y = 0.0$ to 1.0 in steps of 0.2. However, we
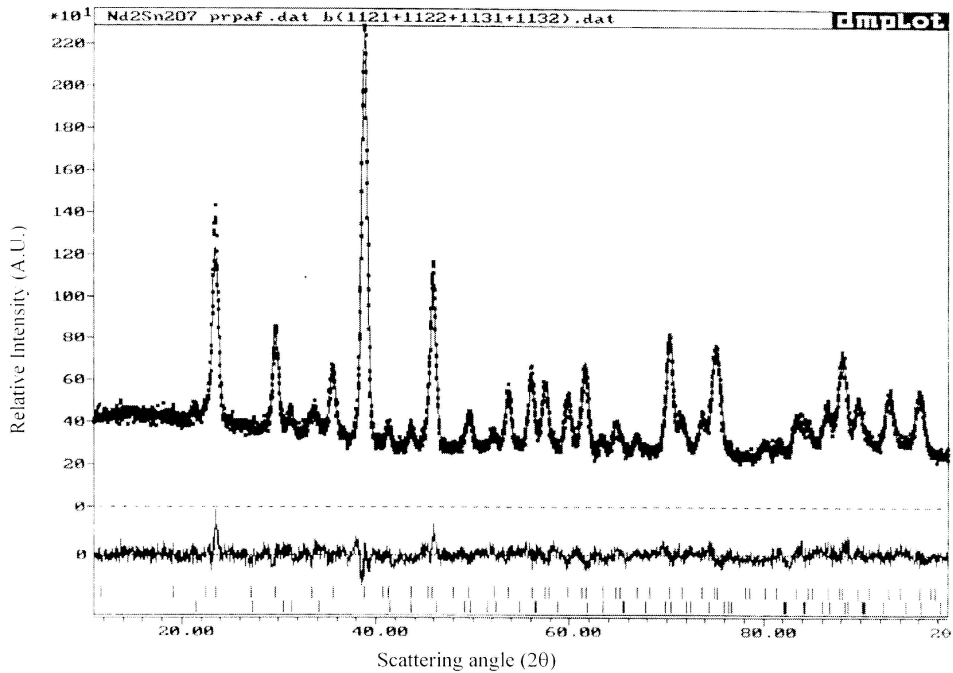

Figure 1. Observed, calculated and difference neutron powder diffraction profiles for $Nd_2Sn_2O_7$.

Table 1. Room temperature structural parameters for stannate–zirconate pyrochlores obtained from a Rietveld-type refinement from powder neutron diffraction data.

Parameters	Content of $y = $ Zr		
	0.0	0.2	0.4
Lattice constant a (Å)	10.564(6)	10.570(1)	10.579(9)
Oxygen positional parameter x	0.3318(1)	0.3317(2)	0.3322(2)
Temperature factors			
B_{Nd}	0.14(5)	0.16(6)	0.20(6)
$B_{\mathrm{Sn}}/B_{\mathrm{Zr}}$	0.48(5)	0.49(6)	0.57(6)
B_{O1}	0.70(3)	0.74(3)	0.69(3)
B_{O2}	0.73(9)	1.0(1)	0.75
Occupancy parameters			
n_{Nd}	0.0833	0.0833	0.0833
n_{Sn}	0.0830(1)	0.0750	0.0690(1)
n_{Zr}	–	0.0083	0.0168(9)
n_{O1}	0.2410(2)	0.2380(1)	0.2430(2)
n_{O2}	0.0404(7)	0.0407(7)	0.0417
R-factors			
R_{p} (%)	5.16	5.87	5.5
R_{wp} (%)	6.48	7.53	7.00
R_{expected} (%)	4.95	5.66	5.15
R_{Bragg} (%)	6.67	8.75	10.00

Parameters without error bars were found not to vary significantly on variation.

have enclosed only two (i.e. parent compound $Nd_2Sn_2O_7$ and ending compound Nd_2SnZrO_7) X-ray diffraction patterns. From the X-ray diffraction patterns, it is observed that there is a broadening in the peak width of X-ray diffraction reflections from composition $Zr = 0.6$. Due to this reason, we have restricted the neutron diffraction study for $y < 0.6$. From table 1, it is also observed that though the lattice parameters show a systematic variation with Zr composition, the variable oxygen parameter x does not show any systematic behavior. The present study indicates that there are only two anion sites, 48f and 8b. This confirms that the 8a site is completely vacant and the structure is a perfectly cubic pyrochlore with space group Fd3m (O_h^7). This observation is similar to the earlier report [6].

The samples are also characterized by employing X-ray diffractogram (XRD) (Phillips model PW-1710), using CuK_α radiation. From the XRD patterns (shown in figures 2a and 2b), it is clear that all the samples are single-phase compounds with fcc structure. In comparison of figures 2a with 2b, there is a broadening in the peak width of X-ray diffraction line for $y = 1.0$. This broadening of the peak would be correlated to the reducing particle size of the compounds. The XRD pattern for $y = 1.0$ shows occurrence of peak at $d = 2.8841$ Å, which may correspond to $(3\,1\,3)$ plane of orthorhombic superlattice. Various pyrochlores have shown occurrence of fluorite or orthorhombic superlattice [7]. The interplaner distance d and the
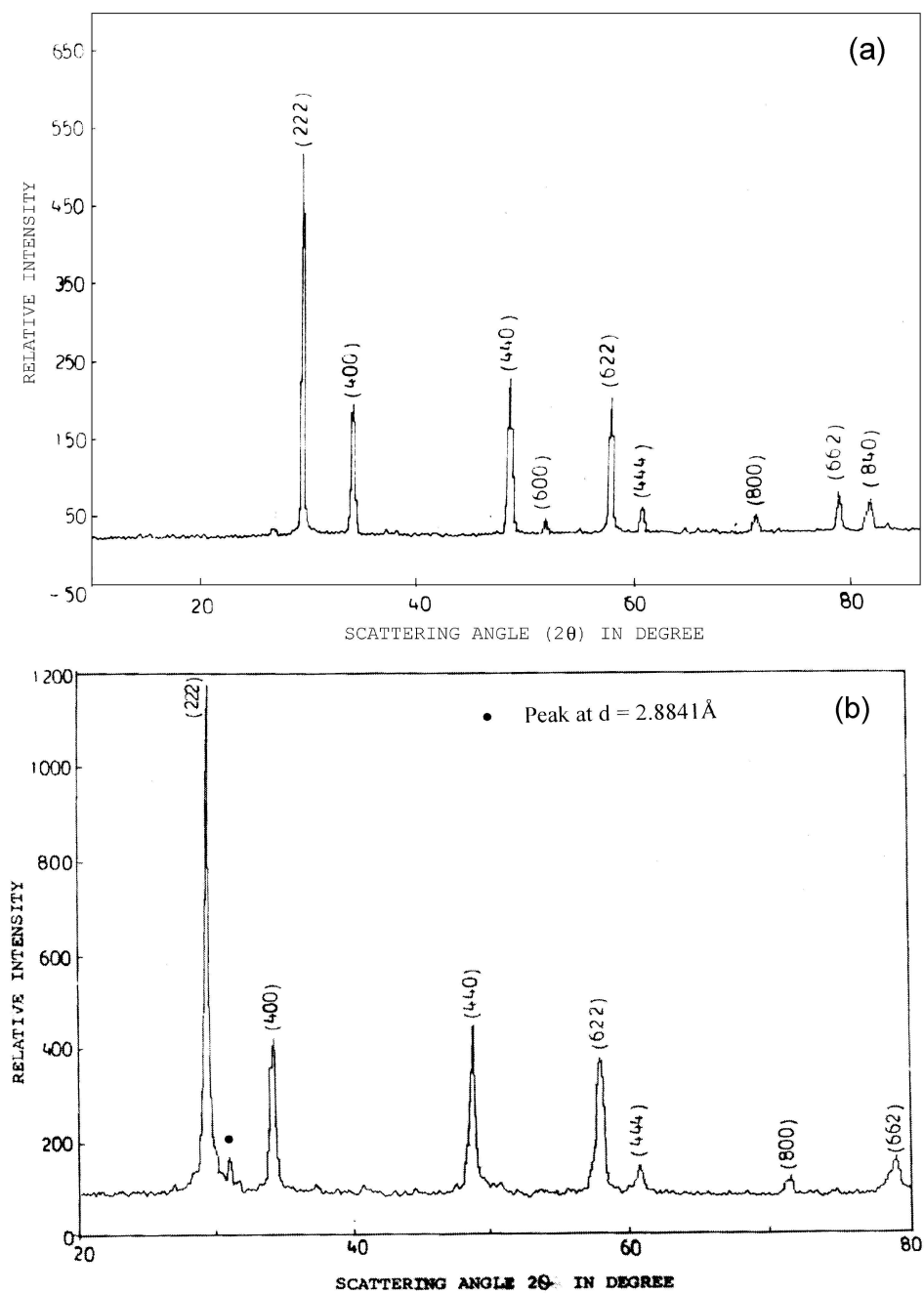
Figure 2. (a) X-ray diffraction pattern for $Nd_2Sn_2O_7$ pyrochlore. (b) X-ray diffraction pattern for Nd_2SnZrO_7 pyrochlore.

average value of lattice parameter a are determined, using the procedure elaborated in ref. [8]. Calculated and observed d values for the characteristic reflections of the pyrochlore structure are in good agreement. Table 2 shows the variation of average lattice parameter (from X-ray diffraction) with composition y. From table 2, it is observed that the lattice parameter a increases with increase in Zr substitution up to $Zr = 0.4$ then decreases and again increases. This increase in lattice parameter may be correlated to the ionic radii of Sn^{4+} (0.69 Å) and that of Zr^{4+} (0.72 Å). Further decrease and increase in values of lattice parameter may be due to changes in occupancy parameters.

The structure factor (F) and hence relative intensity (I/I_0) calculations for X-ray data are performed manually for all the compositions with the intense reflections. While performing these calculations, the positions of A, B, O and O′ sublattices are determined considering oxygen positional parameter $x = 0.375$ and 0.331. Table 3 shows the observed and calculated relative intensities for the composition $Nd_2Sn_2O_7$. From table 3 it is observed that the calculated and observed intensities are in good agreement for $x = 0.331$. The closeness of the observed and calculated intensities indicates that the coordination around A cation is almost a regular cube [5].

Table 2. Average lattice parameters for $Nd_2Sn_{2-y}Zr_yO_7$ pyrochlores system.

Composition (y)	Average lattice parameters (Å)
0.0	10.573
0.2	10.578
0.4	10.582
0.6	10.570
0.8	10.574
1.0	10.578

Table 3. Calculated and observed relative intensities for $Nd_2Sn_{2-y}Zr_yO_7$ system.

					Relative intensity		
					Observed	Calculated	Calculated
Line	$(h\,k\,l)$	P	$F(\times10^5)$	$\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$		for $x = 0.375$	for $x = 0.331$
1	$(2\,2\,2)$	8	26.166	28.24	100	100	100
2	$(4\,0\,0)$	6	12.270	20.64	30	25	28
3	$(4\,4\,0)$	12	20.300	9.226	35	38	35
4	$(6\,2\,2)$	24	14.554	6.230	30	36	36
5	$(4\,4\,4)$	8	9.7614	5.647	7	7	10
6	$(8\,0\,0)$	6	20.300	3.984	3	8	7
7	$(6\,6\,2)$	24	10.680	3.361	10	15	15
8	$(8\,4\,0)$	24	7.589	3.171	7	8	12

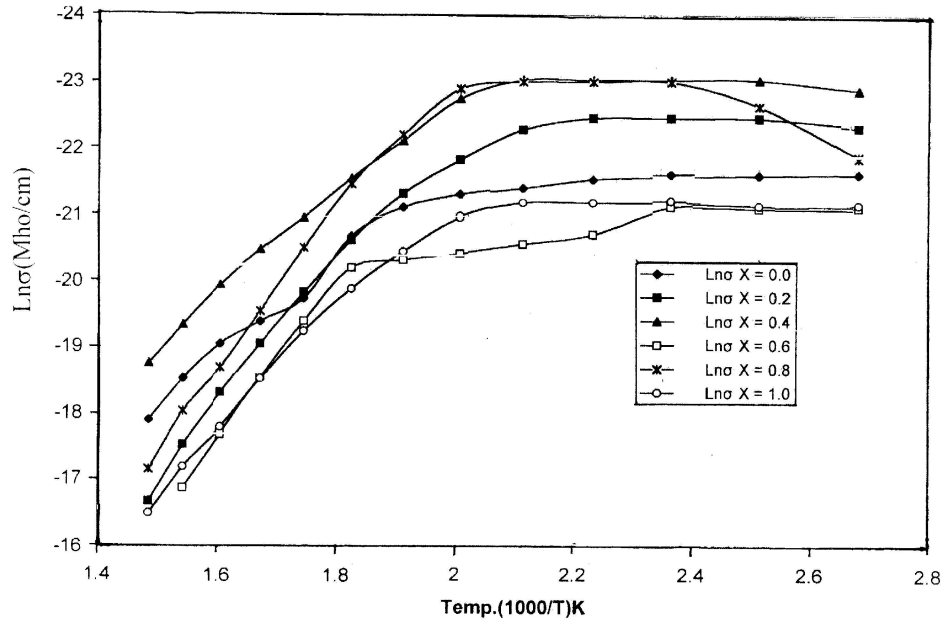**Figure 3.** Variation of $\ln\sigma$ with temperature for Nd$_2$Sn$_{2-x}$Zr$_x$O$_7$ system.

4. Conductivity measurements

Figure 3 shows the variation of $\ln\sigma$ as a function of $1000/T$ for all the compositions of the system. An examination of figure 3 indicates that there are two regions of conduction. Region I occurs below 525 K, while region II occurs at higher temperatures. Regions I and II show an Arrhenius behavior with activation energies characterizing electronic conduction below 525 K and ionic conduction involving oxygen ions at higher temperatures.

5. Complex impedance spectroscopy

As we concluded that for temperatures less than 525 K, the electronic conduction dominates while for temperatures greater than 525 K, the ionic conduction is dominant in the present system. However, earlier investigations on insulating zirconate pyrochlores have shown that a significant amount of electronic conduction may persist in these compounds for temperatures as high as 1273 K, though these are predominantly ionic conductors. The complex impedance plots could be used to separate out these contributions in two separate semicircles. Complex impedance plots for $y = 0.0$ at temperatures above 525 K are shown in figures 4a and 4b. From these plots, it is observed that two semicircles are apparent in all the figures. The semicircle at lower frequency due to grain boundary or micro-chemical inhomogeneity as proposed by Van Dijk *et al* [9], corresponds to the ionic conduction
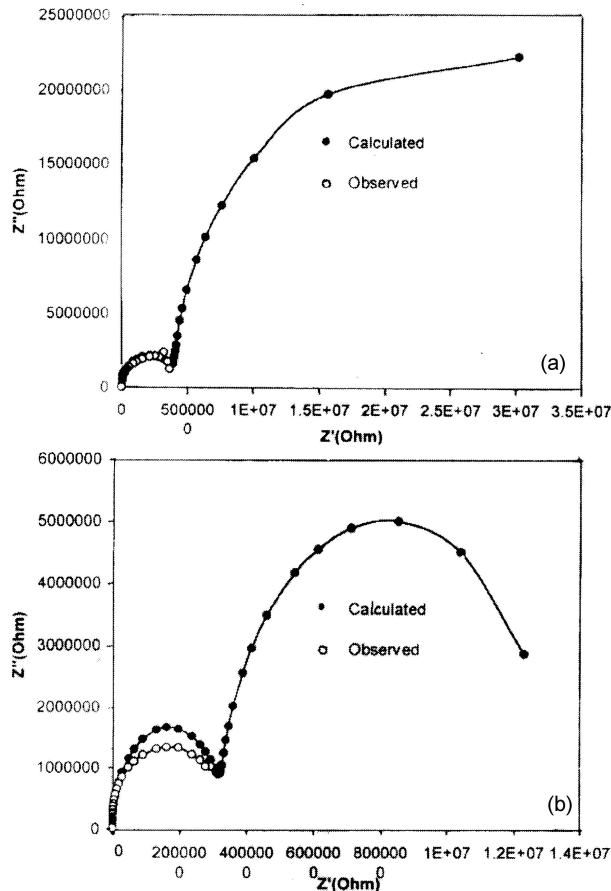
Figure 4. (**a**) Cole–Cole plot for $Nd_2Sn_2O_7$ at $380°C$. (**b**) Cole–Cole plot for $Nd_2Sn_2O_7$ at $430°C$.

contribution. The semicircle occurring at higher frequencies due to the bulk of the grain corresponds to the electronic conduction contribution.

6. Conclusions

The structural investigation on the present system suggests that for $y < 0.6$, the compositions posses the perfect cubic pyrochlore structure with space group Fd3m (O_h^7) and oxygen positional parameter 0.375. For further increase in Zr concentration, orthorhombic superlattice is apparent from the XRD investigations. The investigations on electrical conductivity and complex impedance spectroscopy suggest the existence of grain and grain boundary as two separate elements. The grain boundaries are observed to be highly resistive at low temperatures. As the temperature increases, the oxygen ion conduction is observed to dominate overall conduction process.

References

[1] M A Subramanian, G Aravamudan and G V Subba Rao, *Prog. Solid State Chem.* **15**, 55 (1983)

[2] A B Harker, in *Radioactive waste forms for the future* edited by W Lutze and R C Ewing (North-Holland, Amsterdam, 1988) p. 342

[3] D R Spink and J H Schemel, *J. Nucl. Mater.* **49**, 1 (1973/74)

[4] M A Subramanian, G Aravamudan and G V Subba Rao, *Oxide pyrochlores – A review*

[5] B J Kennedy, Brett A Hunter and Christopher J Howard, *J. Solid State Chem.* **130**, 58 (1997)

[6] Catherine Heremans *et al*, *J. Solid State Chem.* **117**, 108 (1995)

[7] A Manthiram and J Gopalkrishnan, *Indian J. Chem.* **A19**, 1042 (1980)

[8] B D Cullity, *Elements of X-ray diffraction*, second edition (Addition Wesley Publishing Co. Inc. Reading, MA, USA, 1956)

[9] M P Van Dijk *et al*, *Mater. Res. Bull.* **19**, 1149 (1984)